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## Electron microscopic study on pyrolysis of CCA (chromium, copper and arsenic oxide)-treated wood

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### Abstract

The effectiveness of pyrolysis as a possible technique for disposing of CCA (chromium, copper and arsenic oxide)-treated wood was studied. A CCA-treated sample given an extra heat treatment at 450 °C for 10 min was thoroughly investigated in order to establish the details of the reaction in which arsenic is captured in the pyrolysis residue prior to volatilization. Composition and structure of the metal compounds in the pyrolysis residue were examined by transmission electron microscopy (TEM). A large number of particles were found of variable diameter between 10 and 100 nm. The smaller ones were mostly spherical, sometimes faceted. The larger ones were lumpy. CCA compounds and their reaction products like  $\text{Cr}_2\text{As}_4\text{O}_{12}$  and  $\text{As}_2\text{O}_3$  were identified in conventional TEM by selected area electron diffraction. In high resolution, the nanoparticles exhibited lattice fringes as indication of their monocrystalline character, fitting, e.g., the  $d_{210} = 0.204$  nm of Cr. The volatility of arsenic during pyrolysis of CCA-treated wood was measured by XRF (X-ray fluorescence) analysis at temperatures up to 500 °C and at times up to 1 h. Weight change and arsenic content of the pyrolysis residue were measured after dissolution in  $\text{HNO}_3$ . More than 20% of arsenic was already lost at 300 °C, which may have been caused mainly by the volatilization of the unreacted arsenic compound after reduction of As(V) in  $\text{As}_2\text{O}_5$  to As(III) in  $\text{As}_2\text{O}_3$ . Arsenic is probably released as  $\text{As}_4\text{O}_6$ , which is very difficult to capture and toxic. By an additional heat

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treatment, this reduction can be prevented and the dry separation of the metals may be allowed.

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**Keywords:** Waste wood; Recycling; Chromated copper arsenate; Charcoal; Transmission electron microscopy

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## 1. Introduction

Recycling of waste wood is important for the effective utilization of natural resources. In reality, most such wood is incinerated due to the lack of a labour force and systematic approach to demolishing residential houses. The disposal by incineration of waste wood is a practical way to suppress the emission of pollutants and for saving energy. The energy from incineration of waste wood could be converted to a source of heating, although an environmentally benign technology should be developed [1–3].

In the incineration of waste CCA-treated wood, the behavior of the preservative chemicals under thermal conversion should be examined with consideration to the environment [4]. It is said that arsenic compounds change to volatile arsenic or arsenious acids and cause air pollution after burning. On the other hand, chromium and copper compounds are considered to remain in the ash as water-insoluble solids on the heating of CCA-treated wood. It was reported that a strong acid such as sulfuric acid could dissolve and extract CCA compounds which had been fixed in wood. The solvent extraction of CCA chemicals by other type of acids or decomposition by microorganisms has been tried for the efficient disposal of treated products. Recently, carbon dioxide in a supercritical condition was applied to recover CCA chemicals by exploiting its excellent extraction and penetration capacity.

Low-temperature pyrolysis may be one of the promising methods [5–10]. However, these methods are yet to be practically established. A study on pyrolysis of CCA (chromium, copper and arsenic oxide)-treated wood is undertaken. An experimental facility was built to examine the influence of process parameters such as pyrolysis temperature and pyrolysis time in order to maximize the capture of arsenic in wood charcoal along with a high oil yield. The purpose of this research is to study the precipitate distribution and microstructure of CCA in pyrolysis residue and to find the most effective ways of capturing arsenic during pyrolysis.

## 2. Experiment

### 2.1. Set up of apparatus

An experimental facility has been built for the pyrolysis of CCA-treated wood powder. A schematic diagram of the pyrolysis system with a glassware reactor is shown in Fig. 1. The glass reactor holds the sample and the volatile products are

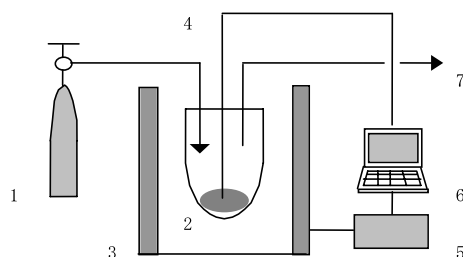


Fig. 1. Experimental setup: (1)  $N_2$  gas feeding system, (2) pear glass reactor, (3) electric furnace (heater), (4) thermocouple, (5) power, (6) computer, (7) gas outlet.

captured before exit. When the sample is pyrolysed, most parts of the reactor are situated inside the heating system. The other end is connected with the inlet tube from a  $N_2$  gas cylinder. The side arm of the glass reactor is connected to a cold trap and to a glass washing bottle.

Inside the cooling trap is a liquid  $N_2$ -cooled acetone solution. The washing bottle contains 30 ml of acetone-based tetra-butyl-ammonium hydroxide (TBAH) with the volume ratio being 2 to 1, which collects arsenic(III) oxides. The reaction temperature was monitored with a thermocouple connected to a temperature controller that regulates the temperature of the heating system. The complete yield balance was determined with this setup.

## 2.2. Materials

The feedstock used in the experiment, supplied by Koshii & Co. Ltd., was Western Hemlock (*Tsuga heterophylla*) treated with type III CCA salt. Type III is a CCA formation containing 45–51% as  $CrO_3$ , 17–21% as  $CuO$  and 30–38% as  $As_2O_5$  [11]. The CCA-treated planks were broken down into chips and milled to powder with a particle size under 100 mesh and mixed sufficiently to minimize the non-uniform distribution of CCA salts in the sample.

## 2.3. Pyrolysis methods

One gram of CCA-treated wood powder was heated in  $N_2$  atmosphere using an electric furnace. The reaction temperature and time were 100–500  $^{\circ}C$  and 10–60 min, respectively, with an in-between heating rate of 3  $^{\circ}C s^{-1}$ .  $N_2$  passed through the accumulated wood charcoal residue and swept away the volatiles to the gas outlet in Fig. 1. The pyrolysis condensates were collected and the remaining gases went through the washing bottle with an acetone-based TBAH solution. The smoke can be characterized as a combination of oil vapor, micron-sized droplets and polar molecules bonded with water vapor.

## 2.4. Analysis

Weight change and arsenic content of the samples were measured by XRF (X-ray fluorescence) after dissolving them in  $\text{HNO}_3$ . The weight change was defined as the percentage ratio of the weight of pyrolysis residue based on the weight of original CCA-treated wood. The reaction time was defined as the time between the sample reaching the desired temperature and the moment it was removed from the reactor. For example, a reaction time of 0 means that after the sample was heated to the desired temperature, it was immediately removed from the reactor.

Changes in arsenic content were defined as the percentage ratio of the arsenic content in the pyrolysis residue based on the arsenic content in the original CCA-treated wood. Composition and structure of the metal compounds in the pyrolysis residue were examined by transmission electron microscopy (TEM; JEOL 2010F with GATAN Imaging Filter and EDS, JEOL 4000EX/II with PEELS).

The weighed sample (0.1 g of pyrolysis residue) was transferred into a kjeldahl flask to prevent loss by volatilization during the dissolution process and 6 ml of  $\text{HNO}_3$  (Nacalai tesque, 65% pure reagent for toxic metal analysis) was added. The flask was heated on a sand bath at 200 °C for 30 min until the sample had dissolved completely. The arsenic in the solution was analyzed using XRF spectrometry (XRF, JSX-3220), which is an excellent method for both qualitative and quantitative analyses of the elements in solid, powder or liquid sample. The quantitative analysis of arsenic was done based on the calibration curve method, where the intensity of the fluorescent radiation allows the determination of arsenate concentration in the sample. In the quantitative analysis, intensities are compared with the standard solution of arsenic. The measurement was repeated three times for accurate analysis and mean values were taken.

## 3. Results

### 3.1. X-ray fluorescence

In Fig. 2, the change in arsenic content as function of temperature is shown for CCA-treated wood after pyrolysis. These results are based on XRF data between 100 and 500 °C. Obviously, 20% of arsenic content is already lost at 300 °C, which may have been caused by the volatilization of unreacted arsenic compound. Thereafter, the remaining reacted arsenic content decreases more or less linearly.

Weight reduction starts long before 300 °C possibly due to the decomposition of hemicellulose. A higher reaction temperature and longer reaction time lead to more weight reduction.

### 3.2. Electron microscopy

In order to evaluate the effect of pyrolysis, we started out by preparing CCA-treated wood samples before and after the extra heat treatment at 450 °C for 10 min.

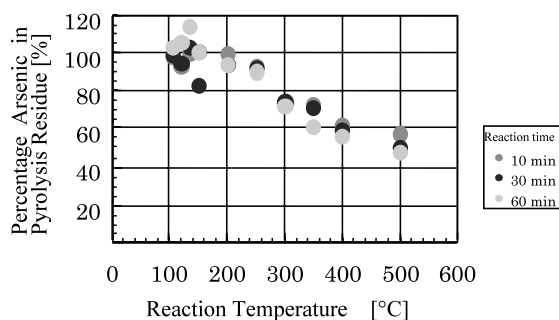


Fig. 2. Percentage change in arsenic content in the pyrolysis residue prior to and during pyrolysis of CCA-treated wood vs reaction temperature (changes in arsenic content (%); the arsenic content in the pyrolysis residue/the arsenic content in the original CCA-treated wood).

As the wood sample was too soft to pulverize, we embedded both samples in Epo and used a microtome with diamond knife to cut foils thin enough for TEM. The sample without the extra heat treatment was showing a nice wood cell structure, but no interesting details linked to CCA treatment. However, after the pyrolysis, a dense collection of nanoparticles was found in the residue as shown in the double image of Fig. 3. The smaller particles were mostly spherical and 10–50 nm in size. A few of them were clearly faceted. Composition determination with EDS was not conclusive. Notwithstanding the fact that the beam of the 2010F microscope can easily be squeezed to below 1 nm, the background spectrum contained almost always Cr, Cu and As. For example, EDS spectra indicated a strong Cu peak even when the spot was put in the background and a Ni grid was used. Subsequently, GIF was used to map these particles with the specific EELS signal for As, Cr and Cu. It was possible to map a larger lump of sample material, indicating a strong C, O and Cr signal, but only a minor contribution in As and Cu. Reproducing these rather noisy graphs is not well feasible.

For that reason, we concentrated more on taking selected area electron diffraction (SAED) patterns combined with bright- and dark-field images (BF/DF) in conventional TEM. In Fig. 4, we have reproduced an image with its corresponding

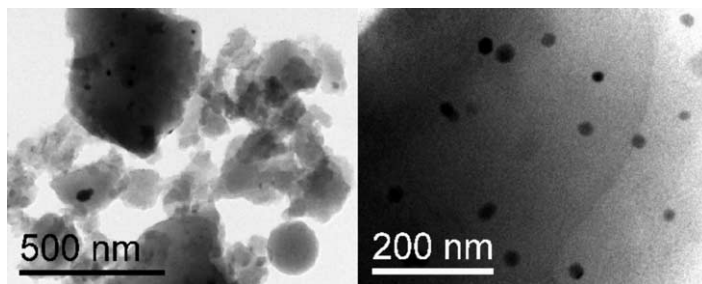


Fig. 3. Pyrolysis residue: CCA-treated wood after an extra heat treatment at 450 °C for 10 min. The sample was crunched, dispersed in isopropanol and a droplet was put on a Lacey carbon foil on a Ni grid. Large lumpy reaction products are depicted on the left and small spherical ones on the right.

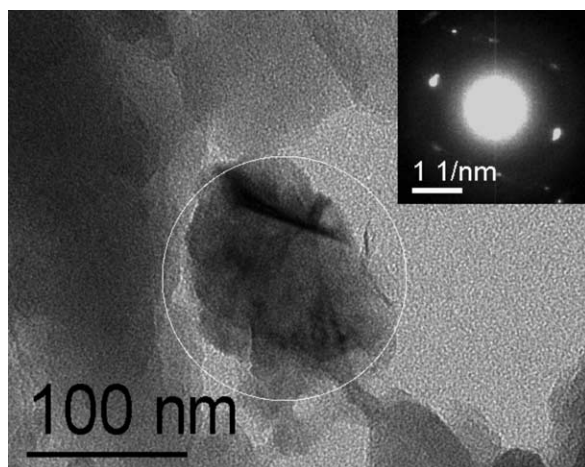


Fig. 4.  $\text{Cr(VI)}_2\text{As(III)}_4\text{O}_{12}$  which could be identified by its strong diffraction spots of (0 0 1) planes with a lattice spacing of  $d_{0\ 0\ 1} = 0.760$  nm as indicated in the inset.

diffraction pattern as inset. The particle turned out to be  $\text{Cr}_2\text{As}_{24}\text{O}_{12}$ . The spots closest to the central beam are the most specific. In this case, they are interpretable as due to (0 0 1) planes with a lattice spacing of  $d_{0\ 0\ 1} = 0.760$  nm. In Fig. 5, we have reproduced another set. This time the particle was confirmed as being an  $\text{As}_2\text{O}_3$  particle with only faintly present diffraction spots corresponding with the (1 1 1) planes with lattice spacing  $d_{1\ 1\ 1} = 0.640$  nm.

In high resolution, one could easily observe lattice fringes in individual particles as proof of their monocrystalline character. An example of such a single crystal with as

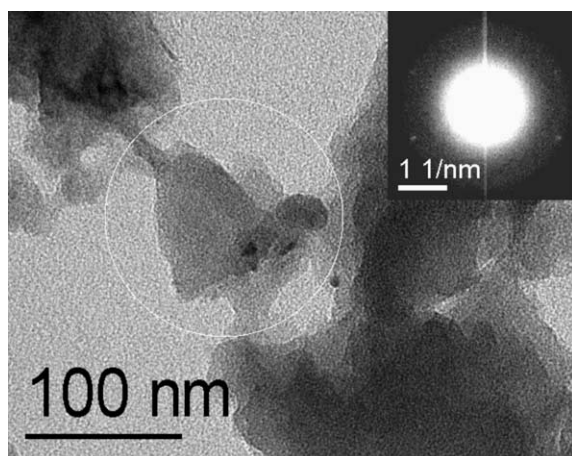


Fig. 5.  $\text{As(III)}_2\text{O}_3$  particle which could be identified by its faint diffraction spots of (1 1 1) planes with a lattice spacing of  $d_{1\ 1\ 1} = 0.640$  nm as indicated in the inset.

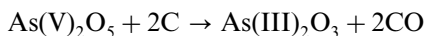


lattice spacing a value of  $d = 0.204$  nm as determined from its FFT could be (2 1 0) spot of Cr but lies also very close to (1 1 1) of Cu with  $d_{111} = 0.208$  nm.

The remainder of the residue consisted of coal in which graphite could be detected with a high tendency of curvature, as depicted in Fig. 6. It would be ultimate to bury the metal-containing particles and especially the As-containing ones under a graphite shell. Patches of metastable diamond were also observed in the remainder of the residue in high-resolution TEM (HRTEM).

#### 4. Discussion

During fixation of CCA salts in wood, oxidation/reduction phenomena play an important role [12–15]. For example, As(III) may react with Cr(VI)O<sub>3</sub> forming the orthorhombic Cr<sub>2</sub>As<sub>4</sub>O<sub>12</sub> salt during pyrolysis as follows:



When the pyrolysis progress, chromium arsenate is decomposed to arsenic pentoxide which is reduced to arsenic trioxide by heating during pyrolysis. Arsenic trioxide starts to sublime at 135 °C [16]. It is gasified as As<sub>4</sub>O<sub>6</sub> at 327 °C [17].

The other possibility is that Cr(III) is formed during the pyrolysis. It may react with As(V)<sub>2</sub>O<sub>5</sub> forming CrAsO<sub>4</sub> salt, which is insoluble in water.

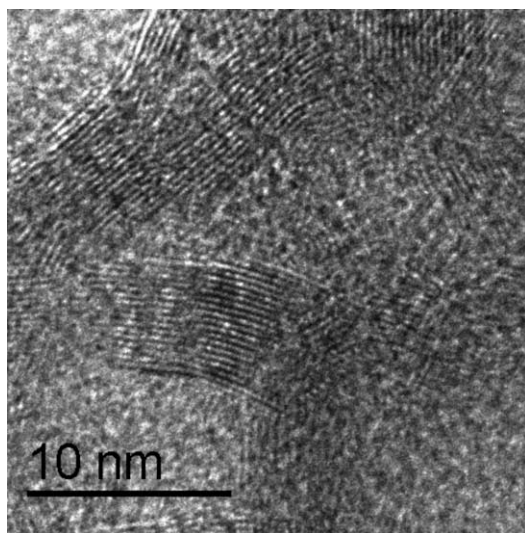


Fig. 6. HRTEM image of typical graphite structured pyrolysis residue. The strong tendency to curve around particles of this carbon part in the residue may be of use in embedding the metal compounds like Cr(VI)<sub>2</sub>As(III)<sub>4</sub>O<sub>12</sub> and As(III)<sub>2</sub>O<sub>3</sub>.



Table 1  
Mechanism of arsenic volatilization during pyrolysis

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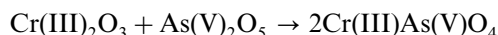
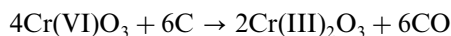
Two types of arsenic compounds

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As<sub>2</sub>O<sub>5</sub>, belonging to one of the three original metal salts, first transforms from As(V)<sub>2</sub>O<sub>5</sub> + 2C → As(III)<sub>2</sub>O<sub>3</sub> + 2CO (150–200 °C). Subsequently, it volatilizes at the initial regime of pyrolysis below *T* = 300 °C as 2As<sub>2</sub>O<sub>3</sub> → As<sub>4</sub>O<sub>6</sub>↑ (327 °C; Helsen and Bulck [17])

Cr<sub>2</sub>As<sub>4</sub>O<sub>12</sub>, the arsenic compound formed after reaction with chromium oxide according to 2Cr(VI)O<sub>3</sub> + 2As(III)<sub>2</sub>O<sub>3</sub> → Cr(VI)<sub>2</sub>As(III)<sub>4</sub>O<sub>12</sub>, first has to decompose during pyrolysis and therefore it volatilizes at higher temperatures as Cr<sub>2</sub>As<sub>4</sub>O<sub>12</sub> → As<sub>2</sub>O<sub>5</sub> (> 700 °C; Kercher and Nagle [18])

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During the conditioning process before the pyrolysis, the As<sub>2</sub>O<sub>5</sub> hardly reacts with Cr(III) remaining in wood as an unreacted compound (Kakitani, 2002).

From this consideration, it is assumed that there are two types of arsenic release during pyrolysis. One is caused by the unreacted arsenic compound (As<sub>2</sub>O<sub>5</sub>) existing in CCA-treated wood, which appears to be released around 150–200 °C (see step around *T* = 200 °C in Fig. 2). The other is caused by the reacted arsenic compound (Cr<sub>2</sub>As<sub>4</sub>O<sub>12</sub>) which appears to be released at higher temperatures (linear part beyond *T* = 300 °C in Fig. 2) [18].

The difference in the amount of unreacted and reacted arsenic compounds in each sample results in a difference in the amount of arsenic release, indicating a possible method to estimate the content of unreacted arsenic compound in the original CCA-treated wood. We assumed that the amount of unreacted arsenic compound in this CCA-treated wood was approximately 20% based on the value at 300 °C, which reduced to 50% at 450 °C (Fig. 2). Our model can best be represented in compact form as shown in Table 1.

## 5. Conclusion

From XRF results, one can conclude that 20% of the original arsenic content is already lost at pyrolysis temperatures below 300 °C (Fig. 2). This may be caused by the volatilization of the unreacted arsenic pentoxide. The reacted chromium arsenate captured in the pyrolysis residue decreases linearly with increasing pyrolysis temperature.

The types of particles observed are the original arsenic pentoxide, arsenic trioxide and the reacted chromium arsenate. EDS scans could distinguish the two arsenic oxides from the reacted arsenate simply by checking the presence of a Cr peak. Structure determination could best be done by making use of SAED patterns in conventional TEM. Lattice fringes as indication of their monocrystalline character were observed in HRTEM.

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